

PATENT SPECIFICATION

(11) 1205 709

NO DRAWINGS

1205 709

- (21) Application No. 30636/68 (22) Filed 27 June 1968
 (31) Convention Application No. 654 705 (32) Filed 20 July 1967 in
 (33) United States of America (US)
 (45) Complete Specification published 16 Sept. 1970
 (51) International Classification C 08 c 11/54
 (52) Index at acceptance C3E 2F7B4A 2F7B4X



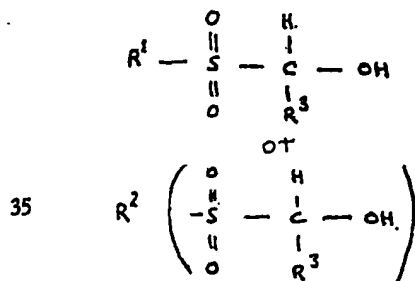
(54) ACCELERATORS FOR SULPHUR-VULCANISING RUBBER

(71) We, UNIROYAL, INC., of Rockefeller Centre, 1230 Avenue of the Americas, New York 10020, State of New York, United States of America, a corporation organised and existing under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with delayed action accelerators for sulphur vulcanizing systems used to vulcanize unsaturated rubbers. In particular the invention relates to the use of organic sulphinic acids and certain salts and derivatives thereof as delayed action accelerators for sulphur vulcanizable compositions.

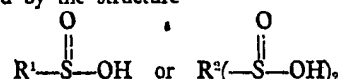
It is an object of the present invention to provide delayed action vulcanization accelerators which exhibit a high degree of scorch safety when relatively high temperature mixing and processing operations are used, but which are effective vulcanization accelerators at higher curing temperatures.

According to the present invention there is provided a sulphur vulcanizable rubber composition which contains (i) an organic sulphinic acid, (ii) a metal salt or amine salt of an organic sulphinic acid, (iii) an aldehyde derivative of an organic sulphinic acid, having the formula



wherein R^1 is a monovalent organic radical, R^2 is a divalent organic radical and R^3 is hydrogen or an organic radical, or (iv) an amine derivative of (iii).

The organic sulphinic acids may be represented by the structure



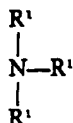
where R^1 is a monovalent organic radical and R^2 is a divalent organic radical. R^1 or R^2 are conveniently substituted or unsubstituted hydrocarbyl groups. The monovalent hydrocarbyl moiety or group may conveniently be an aryl, alkyl, cycloalkyl, aralkyl or alkaryl group. The alkyl group or moiety preferably contains from 1 to 8 carbon atoms and the cycloalkyl group preferably contains from 5 to 8 carbon atoms. The divalent hydrocarbyl moiety may conveniently be alkylene or arylene e.g., methylene, polymethylene, phenylene, biphenylene or naphthylene. The substituents may for example be halo (e.g. chloro or bromo), nitro, or acetamido. R^1 may also be a heterocyclic radical such as a 2-benzothiazyl group. Examples of groups for R^1 thus include phenyl, biphenyl, naphthyl, methyl, butyl, octyl, cyclohexyl, benzyl, tolyl, chlorophenyl, nitrophenyl and acetamidophenyl.

The metal salts of the sulphinic acids defined above which may be used according to the present invention include monovalent and polyvalent metal salts such as sodium, potassium, lithium, calcium, magnesium, aluminium, barium, zinc, copper, nickel, cadmium, cobalt, tin, lead and iron salts.

The amine salts (which term is used herein to include ammonium salts) of sulphinic acids which may be used according to the present invention comprise the reaction products of a sulphinic acid with an organic amine or ammonia. Primary, secondary or tertiary amines may be employed. The amine may have the formula

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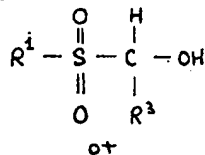
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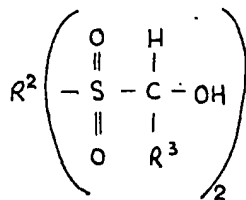
wherein R^1 is as already defined and/or two groups R^1 taken together with the nitrogen atom form a ring.

- 5 Preferred amines include alkyl substituted amines and cycloalkyl substituted amines. The hydrocarbyl groups may carry substituents such as cyano or hydroxyl groups. Specific amines which may be used include methyl-
10 amine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, secondary butylamine, tertiary butylamine, tertiary octylamine, triethylamine, tributylamine, amylamine, hexylamine, octylamine, dodecylamine, octadecylamine, morpholine, piperidine, dimethylamine,
15 ethanolamine, cyanoethylamine, diethylamine, dipropylamines, dibutylamine, laurylamine, cyclohexylamine, dicyclohexylamine, benzylamine, trimethylamine, ethylenediamine, dimethylamino propylamine, piperidine and morpholine.

- 20 The aldehyde derivatives of organic sulphonic acids which may be used are simply derived by reacting an organic sulphonic acid with an aldehyde, preferably formaldehyde. These derivatives are alpha-hydroxy sulphones e.g., those having the formula



or



- 30 where R^1 and R^2 have the meanings given above and R^3 is hydrogen or an organic radical which is preferably a hydrocarbyl group e.g. an alkyl or an aryl group such as methyl, propyl, octyl, phenyl, biphenyl or naphthyl.

- 35 The alpha-hydroxy sulphones may be further reacted with an amine (including ammonia) to form the aldehydeamine derivatives of sulphonic acids. The amine may for example be one of those given above with reference to the amine salts of the sulphonic acids. The amine is preferably ammonia or a primary amine. The nitrogen atom of the amine replaces the hydroxy group of the
40 alpha-hydroxy sulphone.

The following are examples of sulphonic acid compounds which are useful as delayed

action accelerators in the composition of the present invention: p-toluene sulphonic acid, 2,4,5-trichlorobenzene sulphonic acid, zinc benzene sulphinate, calcium benzene sulphinate, barium benzene sulphinate, magnesium benzene sulphinate, lead benzene sulphinate, zinc p-toluene sulphinate, calcium p-toluene sulphinate, barium p-toluene sulphinate, magnesium p-toluene sulphinate, sodium p-toluene sulphinate, t-octylammonium p-toluene sulphinate, n-dodecylammonium p-toluene sulphinate, cyclohexylammonium p-toluene sulphinate, dibutylammonium p-toluene sulphinate, triethylammonium p-toluene sulphinate, t-butylammonium p-toluene sulphinate, n-butylammonium p-toluene sulphinate, dimethylammonium p-toluene sulphinate, zinc salts of mixed toluene sulphonic acids, zinc 2,5-dimethylbenzene sulphinate, cyclohexylammonium-2,5-dimethyl benzene sulphinate, zinc 2-naphthalene sulphinate, cyclohexylammonium-2-naphthalene sulphinate, dicyclohexylammonium p-toluene sulphinate, methylammonium p-toluene sulphinate, zinc salt of meta benzene disulphonic acid, diethylammonium p-toluene sulphinate, cadmium benzene sulphinate, stannous benzene sulphinate, nickelous benzene sulphinate, cupric p-toluene sulphinate, nickelous p-toluene sulphinate, zinc 2,4,5-trichlorobenzene sulphinate, zinc p,p'-oxybis(benzene sulphinate), zinc p-chloro benzene sulphinate, zinc butane-1,4-disulphinate, zinc p-nitrobenzene sulphinate, p-tolyl hydroxymethyl sulphone, p-acetamido benzene sulphonic acid, zinc p-acetamido benzene sulphinate, zinc alpha-toluene sulphinate, reaction product of p-toluene sulphonic acid and ethanolamine, reaction product of p-toluene sulphonic acid and ethylene diamine (2:1), and reaction product of p-toluene sulphonic acid and 3-dimethylamino propylamine.

The delayed action accelerators of the invention may be used in any convenient amount such as from 0.5 to 5 parts by weight based on the weight of the composition, preferably from 1.0 to 2.5 parts by weight.

These accelerators may be made by any convenient conventional method. The salts of the sulphonic acids are usually more stable than the free acids and are hence usually prepared from an alkali metal salt thereof. The alkali metal salts may be prepared by reaction of an organic sulphonyl chloride with sodium sulphite in the presence of aqueous alkali. Treatment of the salt with a mineral acid (e.g. HCl) yields the free sulphonic acid. The alkali metal salt may also be treated with a salt of a mineral acid (e.g. zinc sulphate) to give further metal salts.

Sulphonic acids may also be prepared by reacting aromatic hydrocarbons with sulphur dioxide in the presence of aluminium chloride or by reacting a diazotised aromatic amine

with sulphur dioxide in the presence of a copper catalyst.

5 Treatment of a free sulphinic acid in an organic solvent (such as ethanol) with an amine yields the amine salts. The reaction of the sulphinic acids with aldehydes and subsequently with an amine or ammonia is according to conventional methods.

10 It is preferred to use the free sulphinic acids and their metal salts as delayed action accelerators in the composition of the present invention. These compounds exhibit exceptional scorch safety (based on 270°F. cure data) and are particularly well suited for curing at relatively high temperatures (circa 15 350°F; frequently 300—400°F. or more). Particularly preferred free acids are p-toluene sulphinic acid and 2,4,5-trichlorobenzene sulphinic acid. p-Toluene sulphinic acid appears 20 to be considerably more stable than benzene sulphinic acid.

Several of the ammonium or substituted ammonium salts of the sulphinic acids show a definite advantage over N-cyclohexyl benzothiazole sulfenamide as far as scorch rate at 25 270°F. is concerned.

30 The aldehyde or aldehyde-ammonium (or amine) derivatives generally show scorch safety properties and accelerating characteristics which are intermediate to those of the free acids and the amine salts.

35 The sulphinic acid compounds of the present invention can be used as accelerators in the vulcanization of a wide variety of elastomeric materials such as conjugated diolefin homopolymers and copolymers of conjugated diolefins with copolymerizable monoethylenically unsaturated monomers, including such 40 homopolymers as polyisoprene (natural or synthetic, high cis-content or otherwise), polybutadiene (emulsion or solution-prepared, high cis-content or otherwise), and copolymers like butadiene-styrene copolymer (emulsion or solu-

tion-prepared, stereo-specific or otherwise), butadiene-acrylonitrile copolymer, butadiene-vinylpyridine copolymer, the unsaturated, sulphur-vulcanizable olefin copolymer rubbers, 45 such as terpolymers of ethylene and propylene with such dienes as dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylene norbornene, ethylidene norbornene, and similar non-conjugated dienes (EPDM), and the "butyl" rubbers, that is, rubbery copolymers of isoolefins such as isobutylene with dienes such as isoprene. These may be described in 50 general as unsaturated, sulphur-vulcanizable diene colymer rubbers. The delayed action accelerators of the present invention may be compounded with dienic unsaturated sulphur-vulcanizable rubbers, sulphur, and any desired conventional compounding ingredients usually used in sulphur vulcanizates, all in conventional proportions and in conventional 55 manner. Mixing and shaping of the vulcanizable composition may be accomplished in the conventional manner, and the vulcanization may be accomplished by heating under appropriate conditions usually used for sulphur vulcanization of rubber, the time and temperature of heating being in general inversely 60 related as in conventional practice.

The sulphinic acid compounds may be used as sole accelerators or may be used in combination with other conventional accelerators or vulcanization activators. 65

Vulcanized products prepared from the composition of the present invention are useful in end uses conventional for vulcanized rubber articles such as tyres, belts, hose and footwear. 70

The invention will now be illustrated with reference to the following examples in which all quantities are given as parts by weight. 75

EXAMPLE I

A butadiene-styrene rubber Masterbatch was prepared, combining the following ingredients in a Banbury mixer: 80 85

Oil extended (37.5% oil) butadienestyrene (23% styrene) copolymer rubber	137.5
Zinc oxide	3.0
p-isopropylamino diphenylamine	1.5
High abrasion furnace carbon black	68.0
Wax blend (Sunproof improved)	1.0
Stearic acid	1.0
Polymerized petroleum hydrocarbon plasticizer	3.0
	215.0

Samples of the above masterbatch were then combined with sulphur (2.0 parts) and with a delayed action accelerator of the present invention (1.2 parts) as specified in Table I. Comparisons were also made with commercial accelerators, using 1.75 parts of bis benzothiazole disulphide (MBTS) or N-cyclohexylbenzothiazole sulfenamide (Delac S) 1.25 parts. Portions of each stock were cured for 45 and 90 minutes at 293°F. and for 45 minutes at 350°F. In addition the stocks were subjected to the "Mooney scorch test" and the so-called "scorch time" and "cure rate" were determined. The data are given in Table I.

It can be seen from the data on Table I that the sulphinic acid compounds of the invention are highly effective accelerators at 350°F. and are much less active than the two commercial accelerators at 293°F. The scorch safety of the sulphinic acid derivatives as measured at 270°F. is generally much greater than that of the two commercial accelerators.

EXAMPLE II

In order to evaluate the effectiveness of the sulphinic acid accelerators under a variety of curing conditions rubber compositions were pre-

pared in accordance with the Masterbatch recipe given in Example I and containing 2.0 parts of sulphur and 1.2 parts of a number of sulphinic acid compounds as indicated in Table II. In this case, portions of the stocks were cured at 292°F., 350°F., and 400°F. The "Mooney scorch" was measured at 270°F. The physical properties of the cured vulcanizates are shown in Table II.

EXAMPLE III

Data obtained in a similar study using the Masterbatch recipe given in Example I and employing a number of sulphinic acid compounds are shown in Table III.

It is of particular significance that the sulphinic acids of the invention are much less active as accelerators at lower temperatures (292°F.) than the two standard accelerators (bis benzothiazyl disulphide and N-cyclohexyl benzothiazole sulphenamide) and give highly effective cures at higher curing temperatures (350°F.).

EXAMPLE IV

A number of metal salts of sulphinic acid were similarly studied in the Masterbatch recipe given in Example I. The cure data are shown in Table IV.

TABLE I

Chemical	Scorch Time (270°F.)	Cure Rate (270°F.)	Cure at 293°F.				Cure at 350°F.				
			300% Modulus 45'	90'	Tensile 45'	% Elongation 90'	300% Modulus 45'	Tensile 45'	% Elongation 45'		
None (sulphur alone)	>60'	—	—	150	140	260	1220	1180	650	2320	700
Bis(benzothiazolyl)disulphide (control)	15'30"	4'30"	1190	1280	3070	2640	600	560	1010	2620	660
N-Cyclohexyl benzothiazole sulphenamide (control)	19'15"	4"	1150	1160	3060	2820	600	610	990	2580	680
Zinc benzene sulphinat	39'	>60'	430	860	1980	2580	870	650	1190	2800	620
Zinc p-toluene sulphinat	38'	>60'	440	900	2030	2650	850	660	1200	2840	640
Zinc-p,p'-oxybis(benzene sulphinat)	>60'	—	200	510	700	1970	1000 +	760	1220	3000	610
Zinc p-chlorbenzene sulphinat	47'	60'	310	700	1320	2320	900	690	1240	3130	650
Zinc butane-1,4-disulphinat	>60'	—	200	550	790	2010	1000	730	870	2500	720
Zinc p-nitrobenzene sulphinat	56'	>60'	280	700	1350	2330	900	700	1070	2670	650
p-Toluene sulphinic acid	41'	>60'	460	830	1960	2590	870	600	1130	2870	640
Zinc-alpha-toluene sulphinat	52'	>60'	250	470	1250	2300	950	840	870	2600	760
Reaction product p-toluene sulphinic acid and formaldehyde	34'	>60'	480	930	2290	2930	820	680	1140	2900	680
tert.-Butyl ammonium p-toluene sulphinat	19'	36'	900	1240	2830	2480	670	500	1380	3100	590

TABLE

Chemical	Scorch Time (270°F.)	Cure Rate	Cure at 292°F.					
			300% Modulus		Tensile		Elongation	
			45'	90'	45'	90'	45'	90'
Bis benzothiazole di-sulphide (1.75) (control)	14'30"	3'	1300	1410	3300	3350	600	550
N-Cyclohexyl benzo-thiazole sulphenamide (1.2) (control)	16'30"	3'	1260	1300	3350	2750	610	510
Ammonium p-toluene sulphinat (1.2)	13'31"	32'	450	—	1910	—	860	—
Zinc benzene sulphinat	37'30"	>60'	210	500	150	590	980	860
Calcium benzene sulphinat	>60'	—	30	220	150	610	1000+	960
Barium benzene sulphinat	>60'	—	30	210	150	530	1000+	880
Magnesium benzene sulphinat	60'	—	130	280	230	980	840	940
Lead benzene sulphinat	40'	>60'	190	350	350	1290	1000+	880
Calcium p-toluene sulphinat	51'	>60'	180	380	300	1410	1000+	850
Barium p-toluene sulphinat	53'	>60'	140	160	270	270	1000+	830
Magnesium p-toluene sulphinat	58'	>60'	170	300	270	1100	1000+	860
Lead p-toluene sulphinat	27'	>60'	200	400	480	1600	920	820
Sodium p-toluene sulphinat	30'	>60'	220	500	650	2080	880	780
Zinc 2-benzothiazole sulphinat	57'	>60'	190	310	300	1100	1000+	920
p-Tolyl hydroxymethyl sulphone	30'	>60'	290	660	1070	2070	990	670
t-Octylammonium-p-toluene sulphinat	23'	>60'	310	700	1300	2600	970	740
n-Dodecylammonium-p-toluene sulphinat	35'	>60'	210	400	590	1680	890	860
Cyclohexylammonium-p-toluene sulphinat	21'	37'	380	790	1630	2580	900	380

II

Cure at 350°F.						Cure at 400°F.					
300% Modulus 30' 45'		Tensile 30' 45'		Elongation 30' 45'		300% Modulus 15' 30'		Tensile 15' 30'		Elongation 15' 30'	
1060	1120	3080	2920	640	600	950	960	2640	2410	640	590
920	1000	2720	2820	630	620	860	980	2110	2420	550	600
1020	1120	2550	2610	550	540	1020	1130	2210	2280	530	530
860	950	2660	2700	640	600	960	1100	2420	2300	610	540
660	700	2260	2310	710	670	750	850	2220	2310	680	540
590	660	1920	2190	700	660	730	750	2210	2150	670	630
590	790	2260	2410	730	640	850	910	2440	2500	640	620
790	820	2220	2390	650	610	950	1000	2350	2350	600	580
800	820	2460	2460	660	620	950	990	2040	2100	530	520
650	740	2200	2200	690	630	800	880	2160	2200	600	580
600	720	2210	2400	700	660	890	950	2350	2360	620	600
900	960	2400	2280	600	550	970	1040	2270	2150	570	530
850	990	2370	2450	600	570	1000	1110	2180	2050	540	470
840	700	2210	2410	700	670	700	710	2260	2100	720	670
900	1020	2780	2760	650	620	950	1200	2530	2480	620	540
900	990	2610	2650	630	610	950	1120	2350	2470	580	570
600	520	2200	1900	700	680	850	1300	2240	2400	640	640
860	900	2140	2260	550	540	980	1090	2350	2350	570	540

TABLE

Chemical	Scorch Time (270°F.)	Cure Rate	Cure at 292°F.					
			300% Modulus		Tensile		Elongation	
			45'	90'	45'	90'	45'	90'
Isopropylammonium-p-toluene sulphinate	14'	21'45"	590	1090	2450	2810	750	580
Triethylammonium-p-toluene sulphinate	44'	>60'	250	600	830	2350	960	780
p-Acetamido benzene sulphinic acid	>60'	—	170	310	250	1110	960	880
Zinc p-acetamido benzene sulphinate	>60'	—	10	190	110	500	1000+	950
Dibutylammonium-p-toluene sulphinate	15'	28'	480	980	2280	3150	830	650
t-Butylammonium-p-toluene sulphinate	17'45" 35'15"	Scorch Cure	410	900	1980	2700	820	640
n-Butylammonium-p-toluene sulphinate	16'15" 26'45"	Scorch Cure	420	810	2100	2860	900	920

II (Continued)

Cure at 350°F.						Cure at 400°F.					
300% Modulus 30' 45'		Tensile 30' 45'		Elongation 30' 45'		300% Modulus 15' 30'		Tensile 15' 30'		Elongation 15' 30'	
1020	1100	2700	2590	570	550	1050	1100	2470	2300	560	510
800	900	2560	2650	650	620	1000	1120	2410	2360	590	550
710	840	2370	2320	690	600	980	1010	2360	2350	580	560
540	520	2080	2110	760	710	700	750	2190	2110	690	630
980	1060	2920	2980	660	620	950	1100	2540	2330	600	550
1050	1100	2610	2610	550	560	1100	1180	2300	2170	530	480
810	990	2700	2600	670	590	960	960	2330	2260	580	560

TABLE III

Chemical	Scorch Time	Cure Rate	Cure at 292°F				Cure at 350°F.							
			300% Modulus 45'	90'	Tensile 45'	90'	Elongation 45'	90'	300% Modulus 30'	45'	Tensile 30'	45'	Elongation 30'	45'
Blank (sulphur alone)	>60'	—	—	150	140	260	1220	1180	590	650	1980	2320	740	700
Bis(benzothiazyl)disulfide (control)	13'30"	3'15"	1150	1270	3300	3340	620	670	1010	1040	3000	3130	630	650
N-Cyclohexylbenzothiazole sulphenamide (control)	15'	3'30"	1190	1250	3510	3260	670	610	970	950	3130	3110	710	690
Zinc (mixed toluene) sulphonates	29'	>60'	210	330	780	1500	920	930	920	1010	2630	2810	640	620
Zinc-2,5-dimethyl benzene sulphonate	48'	>60'	140	200	280	650	1070	980	690	800	2230	2530	660	660
Cyclohexylammonium-2,5-dimethyl benzene sulphonate	27'	>60'	210	350	870	1540	830	750	790	840	1910	1980	540	520
Zinc-2-naphthalene sulphonate	46'	>60'	130	200	370	700	1180	1010	600	710	2110	2320	730	660
Cyclohexylammonium 2-naphthalene-sulphonate	25'	>60'	250	440	1100	1810	860	750	800	860	2420	2560	610	600
Dicyclohexylammonium p-toluene sulphonate	17'26"	30'	360	600	1340	1470	710	530	850	960	1820	1820	510	450
Methylammonium-p-toluene sulphonate	45'	>60'	220	400	150	1860	950	810	780	820	2520	2610	680	660
Reaction product of p-toluene sulphonic acid and ethanamine	23'	44'	380	720	1610	2440	820	680	720	820	2710	2550	710	620

TABLE III (Continued)

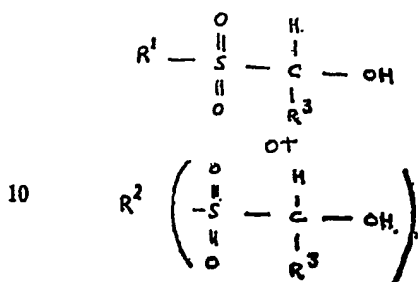
Chemical	Scorch Time	Cure Rate	Cure at 292°F.				Cure at 350°F.			
			300% Modulus 45'	Tensile 90'	Elongation 45'	90'	300% Modulus 30'	Tensile 30'	Elongation 30'	45'
Reaction product of p-toluene sulphonic acid and ethylenediamine (2:1)	15'	22'15"	590	2400	2900	770	1130	3210	3050	610
Diethylamino p-toluene sulphinate	18'30"	31'30"	420	2010	3000	890	1000	2870	2750	610
Mono-n-butylammonium p-toluene sulphinate	18'30"	32'30"	350	1690	2720	880	880	2830	2690	600
Reaction product of p-toluene sulphonic acid and 3-dimethylamino propylamine	12'30"	22'15"	600	2660	3150	780	870	2890	2600	620
Reaction product of p-toluene sulphonic acid and 3-diethylamino propylamine	15'30"	26'	540	2060	2450	750	970	2830	2640	620
Di-n-propylammonium p-toluene sulphinate	19'	32'45"	400	1900	2590	860	970	2750	2880	630
Bis(p-toluene sulphonyl methyl)amine	22'	35'	510	2330	2810	880	1030	2830	2690	620

TABLE IV

Chemical (1-2 parts each)	Cure at 292°F.				Cure at 350°F.				Cure at 400°F.			
	300% Modulus 45' 90'	Tensile 45' 90'	Elongation 45' 90'		300% Modulus 30' 45'	Tensile 30' 45'	Elongation 30' 45'		300% Modulus 15' 30'	Tensile 15' 30'	Elongation 15' 30'	
N-Cyclohexyl benzo- thiazole sulphenamide (control)	1150 1220	3200 3360	630 610		970 1020	3190 3100	560 640		750 810	2690 2590	710 670	
Cadmium benzene sulphinate	250 420	450 1660	960 970		840 950	2660 2690	650 620		900 930	2610 2520	660 610	
Stannous benzene sulphinate	— 300	220 960	1050 910		800 860	1840 2260	530 560		760 910	1900 2100	560 560	
Nickelous benzene sulphinate	200 380	260 1190	1070 890		920 980	2630 2910	640 650		920 1080	2540 2410	630 550	
Cupric p-toluene sulphinate	200 250	240 670	900 740		710 740	2060 2090	640 590		790 850	2250 2250	640 600	
Nickelous p-toluene sulphinate	210 560	420 1950	1010 820		980 1100	2850 2700	620 560		1010 1120	2650 2340	600 550	

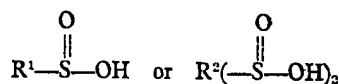
WHAT WE CLAIM IS:—

1. A sulphur vulcanizable rubber composition which contains (i) an organic sulphinic acid, (ii) a metal salt or amine salt of an organic sulphinic acid, (iii) an aldehyde derivative of an organic sulphinic acid, having the formula



wherein R¹ is a monovalent organic radical, R² is a divalent organic radical and R³ is hydrogen or an organic radical, or (iv) an amine derivative of (iii).

2. A composition as claimed in claim 1 wherein the accelerator is a sulphinic acid having the formula



- wherein R¹ is a monovalent organic radical and R² is a divalent organic radical.

3. A composition as claimed in claim 2 wherein R¹ or R² represent substituted or unsubstituted hydrocarbyl groups.

4. A composition as claimed in claim 3 wherein the hydrocarbyl moieties or groups are aryl, alkyl, cycloalkyl, aralkyl or alkaryl groups.

5. A composition as claimed in claim 4 wherein R¹ represents a phenyl, biphenyl, naphthyl, cyclohexyl, benzyl, tolyl, chlorophenyl, trichlorophenyl, nitrophenyl or acetamidophenyl group or an alkyl group having from 1 to 8 carbon atoms.

6. A composition as claimed in claim 3 wherein R¹ represents a heterocyclic group.

7. A composition as claimed in claim 3 wherein R² is an alkylene or arylene group.

8. A composition as claimed in claim 6 wherein R² represents a methylene, polymethylene, phenylene, biphenylene or naphthylene group.

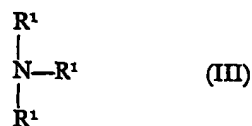
9. A composition as claimed in claim 1 wherein the accelerator is a metal salt of a sulphinic acid as defined in any one of claims 2 to 8.

10. A composition as claimed in claim 9 wherein the salt is a sodium, potassium, lithium, calcium, magnesium, aluminium, barium, zinc, copper, nickel, cadmium, cobalt, tin, lead or iron salt.

11. A composition as claimed in claim 1

wherein the accelerator is an amine (including ammonium) salt of a sulphinic acid as defined in any one of claims 2 to 8.

12. A composition as claimed in claim 11 wherein the amine has the formula



wherein R¹ is as defined in any one of claims 2 to 6 and/or two groups R¹ taken together with the nitrogen atom form a ring.

13. A composition as claimed in claim 11 or claim 12 wherein the amine is an alkylamine or a cycloalkylamine.

14. A composition as claimed in claim 11 or claim 12 wherein the amine is methylamine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, secondary butylamine, tertiary butylamine, tertiary octylamine, triethylamine, tributylamine, amylamine, hexylamine, octylamine, dodecylamine, octadecylamine, morpholine, piperidine, dimethylamine, ethanalamine, cyanoethylamine, diethylamine, dipropylamines, dibutylamine, laurylamine, cyclohexylamine, dicyclohexylamine, benzylamine, trimethylamine, ethylenediamine or dimethylamino propylamine.

15. A composition as claimed in claim 1 wherein the accelerator is an aldehyde derivative of a sulphinic acid as defined in any one of claims 2 to 8.

16. A composition as claimed in claim 15 wherein R³ represents hydrogen.

17. A composition as claimed in claim 15 wherein R³ represents a hydrocarbyl group.

18. A composition as claimed in claim 17 wherein R³ represents an alkyl or aryl group.

19. A composition as claimed in claim 18 wherein R³ represents an alkyl group having from 1 to 8 carbon atoms or a phenyl, biphenyl or naphthyl group.

20. A composition as claimed in claim 1 wherein the accelerator is an amine (including ammonia) derivative of an alpha-hydroxy sulphone as defined in any one of claims 15 to 19.

21. A composition as claimed in claim 20 wherein the amine used to form the derivative is as defined in any one of claims 12 to 14.

22. A composition as claimed in claim 21 wherein the amine is ammonia or a primary amine.

23. A composition as claimed in claim 1 wherein the accelerator is p-toluene sulphinic acid, 2,4,5-trichlorobenzene sulphinic acid, zinc benzene sulphinat, calcium benzene sulphinat, barium benzene sulphinat, magnesium benzene sulphinat, lead benzene sulphinat, zinc p-toluene sulphinat, calcium p-toluene sulphinat, barium p-toluene sulphinat, magnesium p-toluene sulphinat,

- 5 sodium p-toluene sulphonate, t-octylammonium p-toluene sulphonate, n-dodecylammonium p-toluene sulphonate, cyclohexylammonium p-toluene sulphonate, dibutylammonium p-toluene sulphonate, triethylammonium p-toluene sulphonate, t-butylammonium p-toluene sulphonate, n-butylammonium p-toluene sulphonate, dimethylammonium p-toluene sulphonate, zinc salts of mixed toluene sulphinic acid, zinc 2,5-dimethylbenzene sulphonate, cyclohexylammonium-2,5-dimethyl benzene sulphonate, zinc 2-naphthalene sulphonate, cyclohexylammonium - 2 - naphthalene sulphonate, dicyclohexylammonium p-toluene sulphonate, methylammonium p-toluene sulphonate, zinc salt of meta benzene disulphinic acid, diethylammonium p-toluene sulphonate, cadmium benzene sulphonate, stannous benzene sulphonate, nickelous benzene sulphonate, cupric p-toluene sulphonate, nickelous p-toluene sulphonate, zinc 2,4,5-trichloro benzene sulphonate, zinc p,p'-oxybis(benzene sulphonate), zinc p-chloro benzene sulphonate, zinc butane-1,4-disulphonate, zinc p-nitrobenzene sulphonate, p-tolyl hydroxymethyl sulphone, p-acetamido benzene sulphinic acid, zinc p-acetamido benzene sulphonate, zinc alpha-toluene sulphonate, reaction product of p-toluene sulphinic acid and ethanolamine, reaction product of p-toluene sulphinic acid and ethylene diamine (2:1), or the reaction product of p-toluene sulphinic acid and 3-dimethylamino propylamine.
24. A composition as claimed in any one of the preceding claims containing from 0.5 to 5

parts by weight of the delayed action accelerator.

25. A composition as claimed in claim 24 containing from 1.0 to 2.5 parts by weight of the delayed action accelerator.

26. A composition as claimed in any one of the preceding claims wherein the rubber is a conjugated diolefin homopolymer, a copolymer of a conjugated diolefin with one or more copolymerizable ethylenically unsaturated monomers.

27. A composition as claimed in claim 26 wherein the rubber is polyisoprene, polybutadiene, butadiene-styrene rubber, butadiene-acrylonitrile rubber, butadiene vinylpyridine rubber, or terpolymer of ethylene, propylene and a non-conjugated diene, or "butyl" rubber.

28. A composition as claimed in claim 1 substantially as herein described.

29. A composition as claimed in claim 1 substantially as herein described with reference to the foregoing Examples.

30. A vulcanizate whenever prepared by vulcanizing a composition as claimed in any one of the preceding claims.

31. A vulcanizate as claimed in claim 30 in the form of a tyre, belt, hose or footwear.

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